

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO CHEMICAL COMPOUNDS HAVING JUVENILE HORMONE ACTIVITY

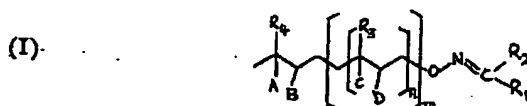
(71) We, A/S CHEMINOVA, a company organized under the laws of Denmark, of 7620 Lemvig, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to chemical compounds having juvenile hormone activity. More particularly, the present invention relates to methods and compositions for the control of insects, and to alkyl, terpenoid and olefinic oximethers of some aryl, pyridyl and aliphatic aldehydes and ketones.

Some compounds exhibit high juvenile hormone activity when applied topically to the insect, stimulating its development and preventing formation of sexually mature adults. Compounds exhibiting this activity may be envisaged as potential insecticides of the third generation.

The compounds of the present invention act selectively on certain insects and, moreover, exhibit high sterilizing properties. The compounds are cheap to prepare and possess higher activity for some insects than many known compounds.

The novel compounds of the present invention are oximethers represented by the following general formula (I)



in which the symbols represents,

A: hydrogen or an alkyl group or an alkoxy group,

B: a hydrogen atom, or,

AB: when taken together, a further single bond between the adjacent carbon atoms, or an oxygen atom,

C: a hydrogen atom,

D: a hydrogen atom, or,

CD: when taken together, a further single bond between the adjacent carbon atoms,

n: zero or one,

m: zero or one,

R₁: a methyl or ethyl group,

R₂: a methyl or ethyl group,

R₃: a hydrogen atom, or an alkyl group with from 1 to 6 carbon atoms,

R₄: an alkyl group, a hydroxy group, a hydroxyalkyl group (e.g. —CH₂OH or —C₂H₄OH), an alkoxy group, an alkoxyalkyl group (e.g. —CH₂—O—CH₃),

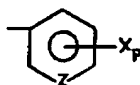
a carboxy group, a carboxyalkyl group (e.g. —CH₂—COOH), a carbalkoxy group i.e., —COOR where R is an alkyl group, a carbalkoxyalkyl group (e.g. —CH₂COOR, where R is an alkyl group), a mono-, di- or tri-halogenalkyl

group, an amide group, a 3,4-methylenedioxypheyl group, or the group with the general formula (II)

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(II)



wherein Z is CH or a nitrogen atom, p is 0 to 3, and X is hydrogen or a substituent such as, for example, NO₂, halogen, OH, CF₃, an alkyl group or an alkoxy group, which substituent X, when p is 2 or 3 may be the same or different.

In all the above definitions, the alkyl, halogenalkyl and alkoxy groups preferably each contain from 1 to 6 carbon atoms. The alkyl is said groups, including the haloalkyl and alkoxy groups, may be straight or branched. As examples may be mentioned methyl, ethyl, propyl, i-propyl, t-butyl, pentyl and hexyl. Preference is given to methyl and ethyl. Preferred compounds of the present invention are compounds of the general formula (I), in which the symbols represents,

A: hydrogen or an alkyl group or an alkoxy group with 1 to 2 carbon atoms

B: a hydrogen atom, or,

AB: when taken together, a further single bond between the adjacent carbon atoms, or an oxygen atom,

C: a hydrogen atom,

D: a hydrogen atom, or,

CD: when taken together, a further single bond between the adjacent carbon atoms,

n: zero or one,

m: zero or one,

R₁: a methyl or ethyl group,

R₂: a methyl or ethyl group,

R₃: a hydrogen atom,

R₄: a carbalkoxy group (—COOR, where R is an alkyl group with from 1 to 6 carbon atoms), a carbalkoxyalkyl group (e.g., —CH₂COOR, where R is an alkyl group with from 1 to 6 carbon atoms), a 3,4-methylenedioxyphenyl group, or a group with the general formula II, wherein Z is CH or a nitrogen atom, p is zero or one, and X is CH₃, when p is one.

Another preferred range of compounds are compounds of the general formula I, in which the symbols have the following meanings:

A: a hydrogen atom,

B: a hydrogen atom,

C: a hydrogen atom, and

D: a hydrogen atom, or

CD: when taken together, a further single bond between the adjacent carbon atoms,

n: zero or one,

m: zero or one,

R₁: a methyl or ethyl group,

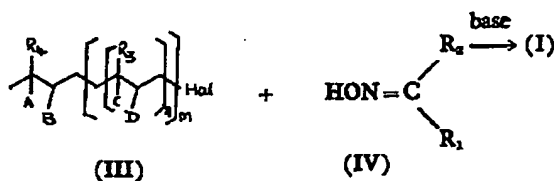
R₂: a methyl or ethyl group,

R₃: a hydrogen atom,

R₄: carbalkoxy group, a carbalkoxyalkyl group, a 3,4-methylenedioxyphenyl group, or a group having the general formula (II) wherein Z is CH or a nitrogen atom, p is zero or one, and X is CH₃, when p is one.

The compounds of the general formula (I) may be prepared, for example, by the following processes:

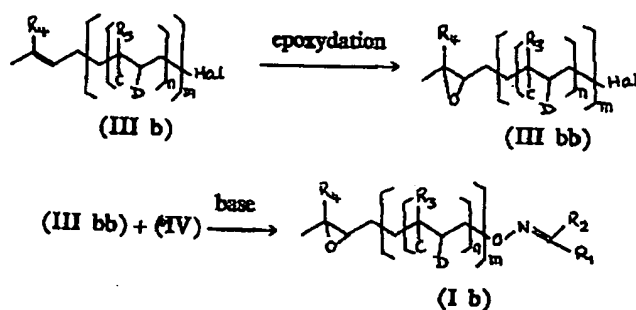
a) By etherformation (O-alkylation) between a compound of the general formula (IV),



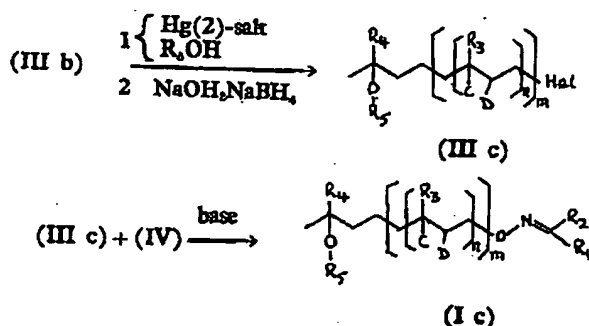
wherein A, B, C, D, n, m, R₄, R₃, R₂, and R₁ have the same meaning as mentioned above and Hal. is chlorine, bromine or iodine.

b) By epoxydation of a compound of the general formula (III b) to form a compound

of the general formula (III bb), followed by an etherformation according to process a) to form a compound of the general formula (I b)



- 5 c) By alkoxylation of a compound of the general formula (III b) to form a compound of the general formula (III c), followed by an etherformation according to process a) to form a compound of the general formula (I c)



wherein R₅ is an alkyl group with from 1 to 6 carbon atoms.

Variations in these main processes due to variation in the starting material may for example be:

- d) Process a), when A B taken together represent a single bond, C D taken together represent a single bond, n is one and m is one.
- e) Process a), when A B taken together represent a single bond, C is hydrogen, D is hydrogen, n is one and m is one.
- f) Process a), when A B taken together represent a single bond and m is zero.
- g) Process a), when A B taken together represent a single bond, n is zero and m is one.
- h) Process b), when C D taken together represent a single bond, n is one and m is one.
- i) Process b), when C is hydrogen, D is hydrogen, n is one and m is one.
- j) Process b), when m is zero.
- k) Process b), when n is zero and m is one.
- l) Process c), when C D taken together represent a single bond, n is one and m is one.
- m) Process c), when C is hydrogen, D is hydrogen, n is one and m is one.
- n) Process c), when m is zero.
- o) Process c), when n is zero and m is one.

The reaction according to process a) between a compound of formula (III) and a compound of formula (IV) is preferably performed in the presence of a base and in an organic solvent, especially potassium hydroxide or sodium hydride in dimethylformamide.

The oximethers of formula (I) can, for example, be prepared according to this process from the chloride, bromide or iodide of the compound of formula (III) by reacting it with a 10% molar excess of the appropriate oxime of formula (IV) and powdered KOH in dimethylformamide. The reaction mixture is stirred for 3 to 20 hours at a temperature between 20 and 60°C, then diluted with water and extracted with ethylether. The organic extract is washed with a 10% KOH solution and finally washed with water. The extract is then dried over anhydrous Na₂SO₄, and the solvent is removed in vacuo. The resulting crude oximether is purified by column chromatography on silica gel, using a benzene/ethylacetate mixture in gradient elution.

The purity can be established to 99% by GLC and combined spectrometric methods.

The epoxidation process according to b) is preferably performed with *m*-chloroperbenzoic acid as the epoxidation agent.

The compounds of formula (III b) can, for example, be epoxidized by reaction with *m*-chloroperbenzoic acid in methylenechloride at 0 to 5°C for two hours. A 10% molar excess of the peracid is used. After the epoxidation is completed, the reaction mixture is poured into an ice-cold 10% aqueous NaHCO₃ solution and is shaken thoroughly. The organic layer is then washed with water, dried over anhydrous Na₂SO₄, and the solvent is removed in vacuo.

The epoxy halogenide of formula (III bb) thus formed is reacted with an oxime of formula (IV) according to process a) as described above, to form a compound of the general formula (I b).

In process c), the terminal alkoxyated compounds of the general formula (I c) can be prepared by the oxymercuration procedure of Brown, H.C. et al.: (J.A.C.S., 91, 5646, (1969)).

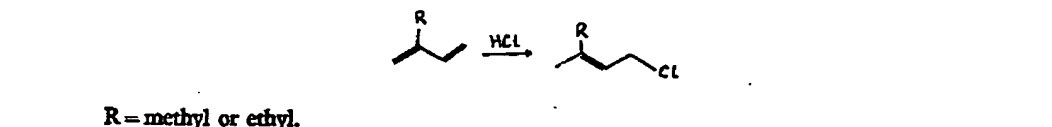
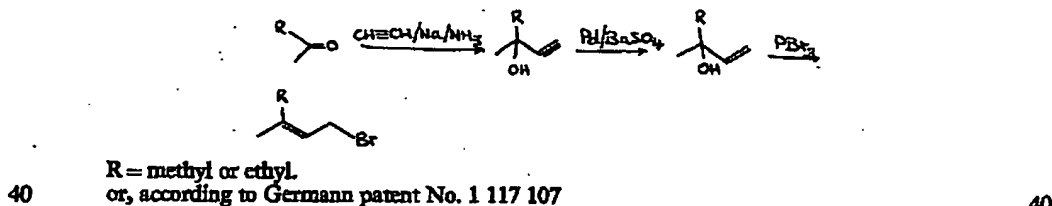
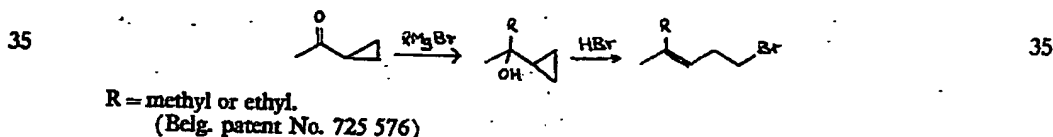
The alkenes of formula (III b) are, for example, treated with mercuric acetate in the appropriate alcohol i.e. the alcohol of formula R₂OH, resulting in the desired alkoxy group in the end product, and the resulting oxymercure intermediate is reduced by adding a solution of NaBH₄ in aqueous NaOH. The mixture is stirred for two hours, until the mercury has coagulated and settled. The reaction product is extracted with *n*-hexane, the extract washed with water, dried over anhydrous Na₂SO₄, and the solvent removed in vacuo. The resulting alkoxyated halogenides of formula (III c) are reacted with oximes of the general formula (IV) according to process a) to form the terminal alkoxyated compounds of the general formula (I c).

The starting materials, oximes of the general formula (IV), may be made by standard methods from the appropriate carbonyl compounds and hydroxylamine hydrochloride.

The starting materials, halogenides of formula (III b), can, when *n*=*m*=1, be either geranyl bromide or -chloride, or citronellyl bromide or -chloride. The halogenides of formula (III b) with shortened chain-length, e.g. *n*=*m*=0 or *n*=0 and *m*=1, are made according to the reaction schemes below.

The Marc Julia synthesis.

(Bull. Soc. Chim. France, 1072, (1960))



All chemical structures are confirmed by a combination of infrared and nuclear magnetic resonance (IR and NMR) data.

In accordance with the present invention, there is provided a method for the control of insects, which comprises contacting the insects, or their eggs or larvae, with a compound selected from those of formula (I) in an amount effective to inhibit the metamorphosis of said insect or to act as sterilizing or ovicidal agent.

Said compound have found to act on species of different orders all over the class of insects, viz. *Coleoptera* (beetles, weevils), *Lepidoptera* (butterflies, moths), *Hemip-*

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tera (bugs, plant lice, scales), *Orthoptera* (grass hoppers), *Dictyoptera* (roaches), and *Diptera* (flies, mosquitoes).

Accordingly, the invention also includes a composition containing a compound of the general formula (I) and a suitable carrier, which composition is suitable for the control of insect pests. To achieve a uniform distribution or application, it is advantageous to employ a composition comprising an inert carrier and, as the essential active ingredient, a compound of the general formula (I).

One method for the control of insects in accordance with the present invention is to apply the composition comprising an inert carrier and a compound of formula (I) to the locus of insect infestation, such as to the plant life on which insects live. These composition can be either solid or liquid.

Solid composition for treating insects can be prepared by incorporating the active ingredient with an inert carrier such as finely divided talc, silica pyrophyllite, diatomite or clay or granular inert carriers, such as the vermiculites.

Liquid compositions can be prepared by mixing the active compound with inert carriers, such as acetone, xylene, peanut oil, cotton-seed oil, sesame oil and other vegetable oils and mineral oils conventionally employed as carriers in insecticidal formulation for application by spraying. Emulsions containing the active ingredient can also be used.

Other ingredients can be present in the composition of the present invention to aid in the effective application of the active ingredient, such as wetting agents, dispersing agents, insect attractants and the like.

The concentration of active ingredient of a compound of formula I in the composition can vary depending on a variety of factors, such as the specific insect involved, the degree of insect infestation, the locus of insect infestation, environment and weather conditions, and type of application device used.

Generally, the composition will contain less than 95% by weight of the active ingredient and more frequently less than 10% by weight.

The compounds of formula (I) are useful insect control agents by virtue of their ability to inhibit the metamorphosis of said insect. The expression "to inhibit the metamorphosis of said insect" as used herein, and in the appending claims, is used to describe the direct effect of the compounds of formula (I) as well as the indirect insecticidal effects of said compounds.

The compounds of formula (I) inhibit metamorphosis of various insect species at different stages, resulting in non-viable intermediates. Depending on the time of application, the compounds of formula (I) show ovicidal, larvicidal or pupicidal effect. When applied to the adult insect, the effect is indirect in the sense that the insect produces non-viable eggs.

The following examples are presented to illustrate the present invention.

Example 1.

Etherformation.

Preparation of benzaldoxime-O-geranyl ether.

A mixture of 24.2 g. (0.20 mol) benzaldoxime and 13.0 g. powdered KOH (85%) in 200 ml. dimethylformamide is stirred for 30 min. 34.6 g. (0.2 mol) geranylchloride is added and the reaction mixture is stirred over night at 50–60°C. 200 ml. water is added to the reaction mixture, which is then extracted with ether. After separation the organic layer is washed with 10% KOH and with water until neutral. The extract is dried over anhydrous Na_2SO_4 and the solvent removed in vacuo. The yield was 38.2 g. of crude oximether, which was purified on silica gel as described below.

Example 2.

Epoxidation.

Preparation of benzaldoxime-O-epoxygeranyl ether.

To a stirred, chilled solution (0°C) of 3.4 g. geranylchloride in 100 ml. methylenechloride is cautiously added 4.5 g. (0.022 mol) 85% m-chloroperbenzoic acid in 30 ml. methylenechloride. The reaction mixture is stirred on an ice-bath for 2 hours, 10% aqueous NaHCO_3 solution is added and the mixture shaken thoroughly. The aqueous layer is extracted with methylenechloride and the combined extracts evaporated in vacuo. The residue is dissolved in ether, washed twice with 10% NaHCO_3 solution and finally twice with water. The etheral extract is dried over anhydrous Na_2SO_4 and evaporated in vacuo. 1.9 g. (0.01 mol) of crude 6,7-epoxygeranylchloride thus obtained is reacted with 1.2 g. (0.01 mol) benzaldoxime in 10 ml. DMF in the presence of 0.7 g. KOH, according to the etherformation described above. For the actual oximether was found, n_D^{25} : 1.5255.

Example 3.

Alkoxylation.

Preparation of benzaldoxime-O-(7-ethoxy-geranyl)-ether.

5 3,4 g. geranylchloride (0,02 mol) is added to a vigorously stirred suspension of
 6,4 g. mercuric acetate in 30 ml. of 99% ethanol at 0°C. One hour after the addition of
 the diene, the mercurial intermediate is reduced by adding 20 ml 0,5 M NaBH₄ in
 3 M NaOH. The mixture is allowed to stir for two hours, until the mercury has coagu-
 10 rated and settled. Then the product is extracted with n-hexane, washed with water until
 neutral, dried over Na₂SO₄ and the solvent is removed in vacuo. 1,1 g. (0,005 mol) of
 crude 7-ethoxy-geranylchloride thus obtained is reacted with 0,6 g. (0,005 mole) benz-
 10 aldoxime in 5 ml. DMF in the presence of 0,35 g. KOH, according to the etherforma-
 tion described above. For the actual oxime ether was found, n_D²⁵: 1,5225.

Example 4.

Chromatography.

15 10 g. crude benzaldoxime-O-geranylether is purified by column chromatography
 on silica gel (0,2—0,5 mm.). The column is filled with 250 g. silica gel and a benzene/
 ethylacetate mixture (4/1 by volume). The elution is started with a 4/1 mixture of
 20 benzene/ethylacetate (200 ml.), and then gradually increasing the concentration of
 ethylacetate during the elution: 3/1 (200 ml.), 7/3 (400 ml.), 3/2 (300 ml.) and
 finally 1/1 (200 ml.). The same procedure was applied to all other compounds.

Example 5.

Formulation.

The active ingredient prepared according to Example 1 can be formulated in the
 following way:

| | | | |
|----|---|--------------------|----|
| 25 | Active ingredient | 10,0 grammes | 25 |
| | 70% Ca-dodecylphenylsulfonate | 5,0 " | |
| | Oleyl-poly(15)ethyleneoxide ether | 5,0 " | |
| | Acetone | ad 100 milliliters | |
| | | (100 g/l a.i.) | |

30 When poured into water, an emulsion is immediately formed, which shortly after
 is transformed into a true solution. Further dilution into any desired concentration can
 be performed.

The water based solution is ready for spraying.

35 In a similar manner to that used in the examples given above, the following com-
 pounds were also prepared.

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TABLE 1

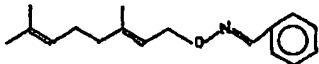

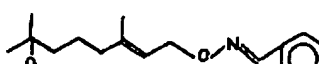
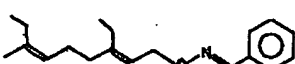

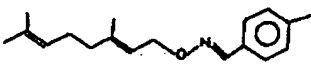
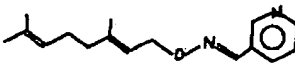
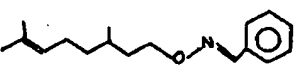
| Comp. No. | Formula and name | n_D^{24} |
|-----------|--|------------|
| 1 | Benzaldoxime-O-geranyl ether.  | 1,5202 |
| 2 | Benzaldoxime-O-6,7-propoxygeranyl ether.  | 1,5255 |
| 3 | Benzaldoxime-O-(7-ethoxy-geranyl)-ether.  | 1,5225 |
| 4 | Benzaldoxime-O-(3-ethyl-7-methyl-2,6-nonadiene-1-yl)-ether.  | 1,5196 |
| 5 | Piperonaloxime-O-geranyl ether.  | 1,5312 |
| 6 | p-Tolualdoxime-O-geranyl ether.  | 1,5233 |
| 7 | 3-Pyridinealdoxime-O-geranyl ether.  | 1,5350 |
| 8 | Benzaldoxime-O-citronellyl ether.  | 1,5206 |

TABLE 1 (Continued)


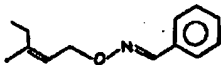

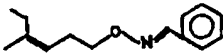
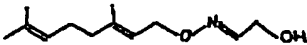
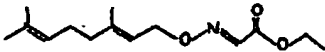
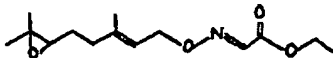
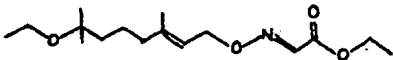
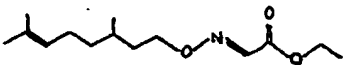
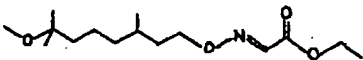
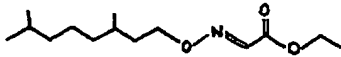
| Comp. No. | Formula and name | n_D^{24} |
|-----------|---|------------|
| 9 | Piperonaloxime-O-(3-methyl-2-pentene-1-yl)-ether.  | 1,5596 |
| 10 | Benzaldoxime-O-(3-methyl-2-pentene-1-yl)-ether.  | 1,5363 |
| 11 | Piperonaloxime-O-(4-methyl-3-hexene-1-yl)-ether.  | 1,5500 |
| 12 | Benzaldoxime-O-(4-methyl-3-hexene-1-yl)-ether.  | 1,5303 |
| 13 | Glycollicaldoxime-O-geranyl ether.  | 1,4905 |
| 14 | Glyoxylic acid ethylester aldoxime-O-geranyl ether  | 1,4682 |
| 15 | Glyoxylic acid ethylester aldoxime-O-(epoxygeranyl)-ether.  | 1,4706 |

TABLE 1 (Continued)

| Comp. No. | Formula and name | n_D^{24} |
|-----------|---|------------|
| 16 | Glyoxylic acid ethylester aldoxime-O-(7-ethoxy-geranyl)-ether  | 1,4702 |
| 17 | Glyoxylic acid ethylester aldoxime-O-citronellyl ether  | 1,4713 |
| 18 | Glyoxylic acid ethylester aldoxime-O-(7-methoxy-citronellyl)-ether  | 1,4722 |
| 19 | Glyoxylic acid ethylester aldoxime-O-(3,7-dimethyl-octyl)-ether  | 1,4453 |

Testing of juvenile hormone activity.

The biological tests are exemplified by tests on *Tenebrio molitor* L., *Galleria mellonella* L. and *Culex pipiens* L. **Tenebrio test:** The material in question is applied topically to the abdomen of 0.5 to 2 hours old pupae of the said specimen, as a solution in acetone. The pupae are held at 27°C and 70% RH, ecodysis occurring 5 to 7 days later. The degree of inhibition of adult characters is referred to an arbitrary scale, a morphologically perfect adult given the character 0%, a perfect second pupa 100%.

Galleria Test: The test is performed on recently laid eggs of *Galleria mellonella* by contact with impregnated filter paper. The data given in table 2, are the amount necessary for preventing eclosion of 50% of the eggs. The amount (IC—50 eclos.) is given in mg./65 cm².

Culex test: The compounds were tested on mature larvae of *Culex pipiens*. The concentration necessary to produce a loss of 50% of the test animals is given in table 2. (IC—50 eclos.) in ppm.

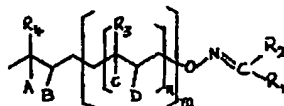
TABLE 2

| Comp. No. | Tenebrio test ID-50 morph. $\mu\text{g/pupa}$ | Galleria test IC-50 eclos. mg/65 cm^2 | Culex test IC-50 eclos. ppm |
|-----------|---|--|-----------------------------------|
| 1 | 0,05 | >10 | <1,0 |
| 2 | >0,1 | — | — |
| 3 | 1,0 | 10 | 10 |
| 4 | 0,01 | — | — |
| 5 | >100 | 10 | 1,0 |
| 6 | 50 | 1,0 | 10 |
| 7 | 10 | — | — |
| 8 | >100 | 10 | <10 |
| 9 | 10 | 10 | 0,02 |
| 10 | >100 | 1,0 | 1,0 |
| 11 | >100 | 5 | 0,5 |
| 12 | >100 | 1,0 | <10 |
| 13 | 50 | — | 10 |
| 14 | 1 | — | 1,0 |
| 15 | 1 | — | 1,0 |
| 16 | 1 | 1 | 1,0 |
| 17 | — | 1,0 | — |
| 18 | — | 1,0 | — |

All compounds made and tested are mixtures of isomers.

WHAT WE CLAIM IS:—

I. A novel chemical compound corresponding to the general formula I



I

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in which the symbols have the following meanings:

A: hydrogen or an alkyl or alkoxy group, and

B: a hydrogen atom, or

AB: when taken together, a further single bond between the adjacent carbon atoms, or an oxygen atom,

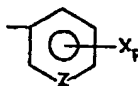
C: a hydrogen atom, and

D: a hydrogen atom, or

CD: when taken together, a further single bond between the the adjacent carbon atoms,

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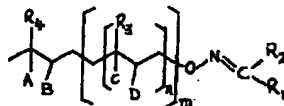
- n : zero or one,
 m : zero or one,
 R_1 : a methyl or ethyl group,
 R_2 : a methyl or ethyl group,
 R_3 : a hydrogen atom, or an alkyl group having from 1 to 6 carbon atoms,
 R_4 : An alkyl group, (a hydroxy group, a hydroxyalkyl group, an alkoxy group, an alkoxyalkyl group, a carboxy group, a carboxyalkyl group, a carbalkoxy group, a carbalkoxyalkyl group, a mono-, di- or tri-halogenalkyl group, an amide group, a 3,4-methylenedioxyphenyl group, or a group having the general formula II



II

wherein Z is CH or a nitrogen atom, p is 0 to 3, and X is a hydrogen atom or at least one substituent which, when p is 2 or 3, may be the same or different.

2. A novel chemical compound corresponding to the general formula I



I

in which the symbols have the following meanings:

- A : an alkyl or alkoxy group, and
 B : a hydrogen atom, or
 AB : when taken together, a further single bond between the adjacent carbon atoms, or an oxygen atom,
 C : a hydrogen atom, and
 D : a hydrogen atom, or
 CD : when taken together, a further single bond between the adjacent carbon atoms,
 n : is zero or one,
 m : is zero or one,
 R_1 : a methyl or ethyl group,
 R_2 : a methyl or ethyl group,
 R_3 : a hydrogen atom, or an alkyl group having from 1 to 6 carbon atoms,
 R_4 : an alkyl group, a hydroxy group, a hydroxyalkyl group, an alkoxy group, an alkoxyalkyl group, a carboxy group, a carboxyalkyl group, a carbalkoxy group, a carbalkoxyalkyl group, a mono-, di- or tri-halogenalkyl group, an amide group, a 3,4-methylenedioxyphenyl group, or a group having the general formula II.

3. A compound as claimed in claim 1 or claim 2 in which the symbol X represents any of the following atoms or groups NO₂, halogen, OH, CF₃, alkyl and alkoxy.

4. A compound as claimed in claim 1 or 2 or 3, in which any of the groups alkyl, halogenalkyl or alkoxy represented by the symbols A, R₂ and X contains from 1 to 6 carbon atoms.

5. A compound as claimed in claim 1 or claim 2, in which a hydroxyalkyl group represented by R₄ is any of the groups —CH₂OH and —C₆H₄OH, an alkoxyalkyl group represented by R₄ is the group —CH₂—O—CH₃, a carboxyalkyl group represented by R₄ is the group —CH₂COOH, and a carbalkoxy or carbalkoxyalkyl group represented by R₄ is any of the groups —COOR and —CH₂COOR, wherein R is an alkyl group having 1 to 6 carbon atoms.

6. A novel compound corresponding to the general formula I in claim 1, in which the symbols have the following meanings:

- A : an alkyl or alkoxy group having 1 or 2 carbon atoms, and
 B : a hydrogen atom, or
 AB : when taken together, a further single bond between the adjacent carbon atoms, or an oxygen atom,
 C : a hydrogen atom, and
 D : a hydrogen atom, or
 CD : when taken together, a further single bond between the adjacent carbon atoms,

n : zero or one,

m : zero or one,

R_1 : a methyl or ethyl group,

R_2 : a methyl or ethyl group,

5 R_3 : a hydrogen atom,

R_4 : a carbalkoxy group, a carbalkoxyalkyl group, a 3,4-methylenedioxyphenyl group, or a group having the general formula II, wherein Z is CH or a nitrogen atom, p is zero or one, and X is CH₃, when p is one.

10 7. A novel compound corresponding to the general formula I in claim 1, in which the symbols have the following meanings:

A: a hydrogen atom,

B: a hydrogen atom,

C: a hydrogen atom, and

D: a hydrogen atom, or

15 CD: when taken together, a further single bond between the adjacent carbon atoms,

n : zero or one,

m : zero or one,

R_1 : a methyl or ethyl group,

R_2 : a methyl or ethyl group,

20 R_3 : a hydrogen atom,

R_4 : a carbalkoxy group, a carbalkoxyalkyl a 3,4-methylenedioxyphenyl group, or a group having the general formula II, wherein Z is CH or a nitrogen atom, p is zero or one, and X is CH₃, when p is one.

25 8. A compound according to claim 1 or claim 2, which is benzaldoxime-O-geranyl ether.

9. A compound according to claim 1, or claim 2 which is benzaldoxime-O-6,7-epoxygeranyl ether.

10. A compound according to claim 1 or claim 2, which is benzaldoxime-O-(7-ethoxy-geranyl)-ether.

30 11. A compound according to claim 1 or claim 2, which is benzaldoxime-O-(3-ethyl-7-methyl-2,6-nonadiene-1-yl)-ether.

12. A compound according to claim 1 or claim 2, which is piperonaloxime-O-geranyl ether.

35 13. A compound according to claim 1 or claim 2, which is p-tolualdoxime-O-geranyl ether.

14. A compound according to claim 1 or claim 2, which is 3-pyridinealdoxime-O-geranyl ether.

15. A compound according to claim 1 or claim 2, which is benzaldoxime-O-citronellyl ether.

40 16. A compound according to claim 1 or claim 2, which is piperonaloxime-O-(3-methyl-2-pentene-1-yl)-ether.

17. A compound according to claim 1 or claim 2, which is benzaldoxime-O-(3-methyl-2-pentene-1-yl)-ether.

45 18. A compound according to claim 1 or claim 2, which is piperonaloxime-O-(4-methyl-3-hexene-1-yl)-ether.

19. A compound according to claim 1 or claim 2, which is benzaldoxime-O-(4-methyl-3-hexene-yl)-ether.

20. A compound according to claim 1 or claim 2, which is glycollicaldoxime-O-geranyl ether.

50 21. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-geranyl ether.

22. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-(epoxygeranyl)-ether.

55 23. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-(7-ethoxy-geranyl)-ether.

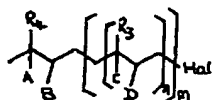
24. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-citronellyl ether.

25. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-(7-methoxy-citronellyl)-ether.

60 26. A compound according to claim 1 or claim 2, which is glyoxylic acid ethylester aldoxime-O-(3,7-dimethyl-octyl)-ether.

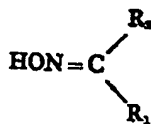
27. A process of preparing a chemical compound of the general formula I as defined in claim 1, in which

a) a compound of the general formula III



III

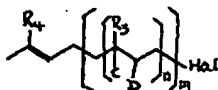
is reacted with a compound of the formula IV



IV

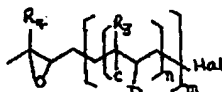
- 5 preferably in the presence of a base, in which formulae A, B, C, D, n, m, R₄, R₃, R₂ and R₁ have the same meaning as indicated in claim 1, and Hal is a halogen atom, preferably a chlorine, bromine or iodine atom, or
b) a compound of the general formula IIIb

5



IIIb

is epoxidized to form a compound of the general formula IIIbb

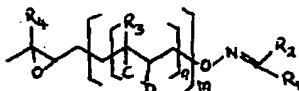


IIIbb

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which is then reacted with a compound of general formula IV, according to process a), to form a compound of general formula Ib

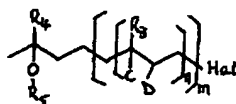


Ib

15

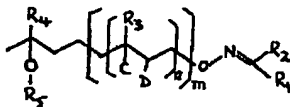
- in which formulae C, D, n, m, R₄, R₃, R₂, R₁ and Hal have the above meaning, or
c) a compound of the general formula IIIb, indicated above, is alkoxylated to form a compound of the general formula IIIc

15



IIIc

which is then reacted with a compound of general formula IV, according to process a), to form a compound of general formula Ic



Ic

20

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in which formula C, D, n, m, R₄, R₃, R₂, R₁ and Hal have the above meaning, and R₅ is an alkyl group having from 1 to 6 carbon atoms.

28. A process as claimed in claim 27a), in which the reaction is performed in the presence of a base and in an organic solvent, preferably potassium hydroxide or sodium hydride in dimethylformamide.

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29. A process as claimed in claim 27b), in which the epoxidation is carried out with *m*-chloroperbenzoic acid as the epoxidation agent.
- 5 30. A process as claimed in claim 27c), in which the compound of formula IIIb is reacted with a mercuric salt in an alcohol of formula R_3OH , wherein R_3 has the meaning stated in claim 27c), and the resulting oxymercuric intermediate product is reduced to form the compound of formula IIIc. 5
31. A process as claimed in claim 30, in which the reduction of the oxymercuric intermediate is performed by means of $NaBH_4$ in aqueous sodium hydroxide.
- 10 32. A process of preparing a chemical compound of general formula I as defined in claim 1, substantially as described, with special reference to the Examples 1 to 3 and to the variation stated on pages 6—7. 10
33. A composition for the control of insects, which comprises a compound of the general formula I, as defined in any of the claims 1 to 6 together with a carrier for said compound.
- 15 34. A composition according to claim 33, which as an active ingredient contains a compound as stated in any of the claims 8 to 26. 15
35. A composition for the control of insects, substantially as described, with special reference to Example 5.
- 20 36. A method for the control of insects which comprises contacting insects, or their eggs or larvae with a composition as claimed in any of the claims 33 to 35. 20

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